

Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

July 1, 2004 – September 30, 2004

Prepared by:

Gary M. Blythe

October 2004

Cooperative Agreement No: DE-FC26-04NT41992

**URS Corporation
9400 Amberglen Boulevard
Austin, Texas 78729**

Prepared for:

Bruce Lani

National Energy Technology Laboratory
U.S. Department of Energy
626 Cochran's Mill Road
Pittsburgh, Pennsylvania 15236

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT41992, “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” during the time-period July 1, 2004 through September 30, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being cofunded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Energy, and Duke Energy. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months or longer at each of two sites to provide longer-term catalyst life data. Pilot-scale wet FGD tests will be conducted periodically at each site to confirm the ability to scrub the catalytically oxidized mercury at high efficiency. The pilot wet FGD system will also be used downstream of catalysts currently being tested as part of another cooperative agreement (DE-FC26-01NT41185). The catalyst pilot units to be used on project 41992 have been in use on project 41185; pilot catalyst testing on project 41992 will commence as the catalyst tests for project 41185 are completed.

This is the third reporting period for the subject Cooperative Agreement. During this period, project efforts included completing the laboratory testing to determine the activity of candidate catalysts at simulated Monticello Plant conditions, and conducting pilot wet FGD tests. The pilot wet FGD tests were conducted at two sites, one being downstream of the oxidation catalyst pilot unit at Coal Creek Station (Site 1 for project 41185) and the other being downstream of the electrostatic precipitator (ESP) at Duke Energy’s Marshall Station. This Technical Progress Report describes the latest bench-scale catalyst test results, and results of the pilot wet FGD tests conducted at Coal Creek Station. The Marshall Station tests were just completed in September, and test results are not yet available to report.

TABLE OF CONTENTS

	Page
Disclaimer	iii
Abstract	iv
Introduction.....	6
Executive Summary.....	8
Summary of Progress	8
Problems Encountered.....	8
Plans for Next Reporting Period.....	8
Prospects for Future Progress	9
Experimental	10
Results and Discussion	11
Laboratory Evaluation of Candidate Catalysts	11
Pilot Wet FGD Tests at CCS.....	13
Conclusion	19
References	20

INTRODUCTION

This document is the quarterly Technical Progress Report for the project “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” for the time-period July 1, 2004 through September 30, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Energy, and Duke Energy. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury is removed in the wet FGD absorbers and mostly co-precipitates with and/or adsorbs on the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months or longer at each of two sites, to provide longer-term catalyst life data. Pilot-scale wet FGD tests will be conducted periodically at each site to confirm the ability to scrub the catalytically oxidized mercury at high efficiency. The pilot wet FGD system will also be used downstream of catalysts currently being tested as part of another cooperative agreement (DE-FC26-01NT41185). The catalyst pilot units to be used on project 41992 have been in use on project 41185; pilot catalyst testing on project 41992 will commence as the catalyst tests being conducted as part of project 41185 are completed.

Four utility team members are providing project host sites for testing. GRE is providing a test site at their Coal Creek Station (CCS), which fires North Dakota lignite. City Public Service of San Antonio (CPS) is providing a test site at their J.K. Spruce Plant, which fires Powder River Basin (PRB) subbituminous coal. Both CCS and Spruce are currently hosting mercury oxidation catalyst pilot tests as part of project 41185. They will also host pilot FGD tests downstream of the catalysts as part of the current, 41992 project.

For the current project, TXU will be hosting pilot catalyst tests and intermittent wet FGD pilot tests at their Monticello Station, which fires a Texas lignite/Powder River Basin (PRB) coal blend. The TXU test program will commence after the current testing at CCS is completed, in the fall of 2004. Duke Energy was also to host oxidation catalyst pilot and wet FGD pilot tests at one of their sites firing low-sulfur Eastern bituminous coal. However, both of their candidate sites that are having wet FGD retrofitted but not selective catalytic reduction (SCR) were measured to have low elemental mercury concentrations in their flue gas downstream of the particulate control device. Consequently, Duke Energy has decided not to host oxidation catalyst pilot tests, although they did host pilot wet FGD tests to determine the ability to scrub the highly oxidized mercury content of the particulate control outlet flue gas at their Marshall Station.

URS and EPRI are in discussions with another utility that fires a low-sulfur Eastern bituminous coal about hosting oxidation catalyst tests. It is hoped that this new host site and project co-funder can be announced next quarter. Assuming these negotiations are successful, oxidation

catalyst pilot tests will commence after the current testing at Spruce is completed, around the beginning of calendar year 2005.

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, July 1, 2004 through September 30, 2004, is the third technical progress report period for the project. Efforts over the current period included laboratory testing to determine the activity of candidate catalysts at simulated Monticello conditions, and completing pilot wet FGD system tests at two sites.

In July, wet FGD pilot tests were conducted downstream of the catalyst pilot unit being operated at CCS as part of another DOE-funded project (DE-FC26-01NT41185), to determine how effectively the catalytically oxidized mercury will be scrubbed. The oxidation catalyst pilot unit was shut down in late September, and that pilot unit was shipped to Monticello in early October. Plant staff are installing it adjacent to the 3C induced draft (ID) fan on Unit 3.

Also, after the pilot wet FGD tests were completed at CCS, the wet scrubber pilot was shipped to Duke Energy's Marshall Station, where baseline (no mercury oxidation catalyst upstream) mercury removal tests were conducted. These tests were conducted in August and September.

Problems Encountered

Duke Energy was also to host oxidation catalyst pilot and wet FGD pilot tests at one of their sites firing low-sulfur Eastern bituminous coal. They had two candidate sites for low-temperature mercury oxidation catalysts: plants that are having wet FGD but not selective catalytic reduction (SCR) unit retrofitted. Wet FGD is required to remove mercury oxidized across the catalysts, but SCR would likely make a separate mercury oxidation catalyst unnecessary for most bituminous coals, due to observed mercury oxidation across SCR catalysts in this type of service. However, both candidate sites were measured to have low elemental mercury concentrations in their flue gas downstream of the particulate control device. Consequently, Duke Energy has decided not to host oxidation catalyst pilot tests, although they did host pilot wet FGD tests to determine the ability to scrub the highly oxidized mercury content of the particulate control outlet flue gas at their Marshall Station.

URS and EPRI are in discussions with another utility that fires low-sulfur Eastern bituminous coal about hosting oxidation catalyst tests. It is hoped that this new host site and project co-funder can be announced next quarter. Assuming these negotiations are successful, oxidation catalyst pilot tests will commence after the current testing at Spruce is completed, around the beginning of calendar year 2005.

There were no other significant problems encountered during the reporting period.

Plans for Next Reporting Period

During the next reporting period (October 1 through December 31, 2004), pilot-scale wet FGD tests will be conducted downstream of oxidation catalysts being operated at Spruce as part of project DE-FC26-01NT41185, to determine how effectively the catalytically oxidized mercury will be scrubbed there. The oxidation catalyst pilot unit from CCS will be installed at Monticello.

Four catalysts will be procured and installed in the pilot unit, and catalyst testing should commence in late November or early December.

Prospects for Future Progress

During the next reporting period (January 1 through March 31, 2005), catalysts will be evaluated for elemental mercury oxidation activity at Monticello through routine (~bimonthly) evaluation trips. Intensive gas characterization efforts and initial wet FGD pilot testing should occur during the quarter. Also during the quarter, the oxidation catalyst pilot unit currently at CPS' Spruce Plant will be shut down and moved to a new site, firing low-sulfur Eastern bituminous coal.

EXPERIMENTAL

The work being conducted as part of this project will use three different experimental apparatus types. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated), the first of which is currently located at GRE's CCS Station in North Dakota. A second, nearly identical pilot unit is currently located at CPS' Spruce Plant. During the course of this project, these two pilot units will be relocated and installed at TXU Energy's Monticello Plant and at a Duke Energy plant, respectively.

Each pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports as part of the ongoing 41185 project^{1,2,3,4}. The activity of these catalysts is determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report⁵. Periodically, the analyzer results are verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The second experimental apparatus is a bench-scale test unit that is used to evaluate the activity of candidate catalyst samples under simulated flue gas conditions. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports for the 41185 project^{3,4}.

The third experimental apparatus is a pilot-scale wet FGD unit that is being designed and fabricated as part of the current, 41992 project, to allow the measurement of how effectively catalytically oxidized mercury can be scrubbed. The pilot unit was designed to treat the flue gas from one of four catalyst chambers on either of the mercury oxidation catalyst pilot units. The design basis and a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system were included in a previous technical progress report for this project.⁶

RESULTS AND DISCUSSION

This section provides details of technical results available from the current reporting period, July 1, 2004 through September 30, 2004. Results include laboratory activity screening of candidate catalyst materials for the upcoming pilot tests at Monticello, and pilot wet FGD test results from downstream of the oxidation catalysts at CCS. The results of wet FGD tests conducted at Marshall Station in August and September are not yet available.

Laboratory Evaluation of Candidate Catalysts

Laboratory evaluation of candidate catalyst materials at simulated Monticello Station Unit 3 conditions was completed during the quarter. Two catalyst materials were repeat tested because of anomalous results from previous testing: palladium catalyst from Sud-Chemie Prototech, and an SCR catalyst from Mitsubishi Heavy Industries.

Table 1 shows the simulation gas species concentrations, and Table 2 shows the results of tests conducted. All of the results shown are based on the use of KCl solutions in the Hg analyzer impinger train when measuring elemental mercury concentrations downstream of the catalysts.

Table 1. Target Simulation Gas Composition for Monticello Laboratory Tests

Species	Concentration
Hg ⁰	45-57 µg/Nm ³
SO ₂	600 ppmv
HCl	1 ppmv
NO _x	400 ppmv
H ₂ O	15%
CO ₂	12%
O ₂	6%
N ₂	Balance

Table 2. Laboratory Catalyst Activity Test Results, July Through September 2004

Catalyst	Core Length, in.	Cell Pitch, cpsi	No. of Cells in Core	Flow Rate, L/min	Area Velocity, sft/hr	Hg Concentration (mg/Nm ³)		Hg ⁰ Oxidation, %
						Inlet Total	Outlet Hg ⁰	
Prototech Pd #1 Repeat	1.02	64	14	0.64	29	100	0.84	99
Prototech Pd #1 Repeat	1.02	64	14	1.00	45	62.2	3.75	94
Prototech Pd #1 Repeat	1.02	64	14	1.41	63	43.3	4.18	90
MHI SCR Repeat	1.04	47	8	0.64	48	78.9	7.94	90
MHI SCR Repeat	1.04	47	8	1.00	76	61.7	8.53	86
MHI SCR Repeat	1.04	47	8	1.41	107	37.4	7.45	80

Figure 1 shows a plot of the palladium data, with elemental mercury oxidation across the catalyst cores on the “Y” axis and the effective catalyst area velocity on the “X” axis. Also plotted are data from previous quarters for the Prototech, Johnson Matthey, and Supplier #2 Pd #1 cores, so the results for all three potential suppliers of Pd #1 can be visually compared. Originally, the middle data point for the Prototech Pd #1 appeared to be an outlier, as the oxidation should gradually drop with increasing area velocity, and the data at the middle area velocity should not show a lower oxidation percentage than the data at the highest area velocity. The retest results show the expected trend of activity decreasing as area velocity increases. With these retest data, the measured performance of the catalysts from the three potential sources for Pd #1 falls within a relatively narrow band, indicating there is not much difference in activity between the three sources.

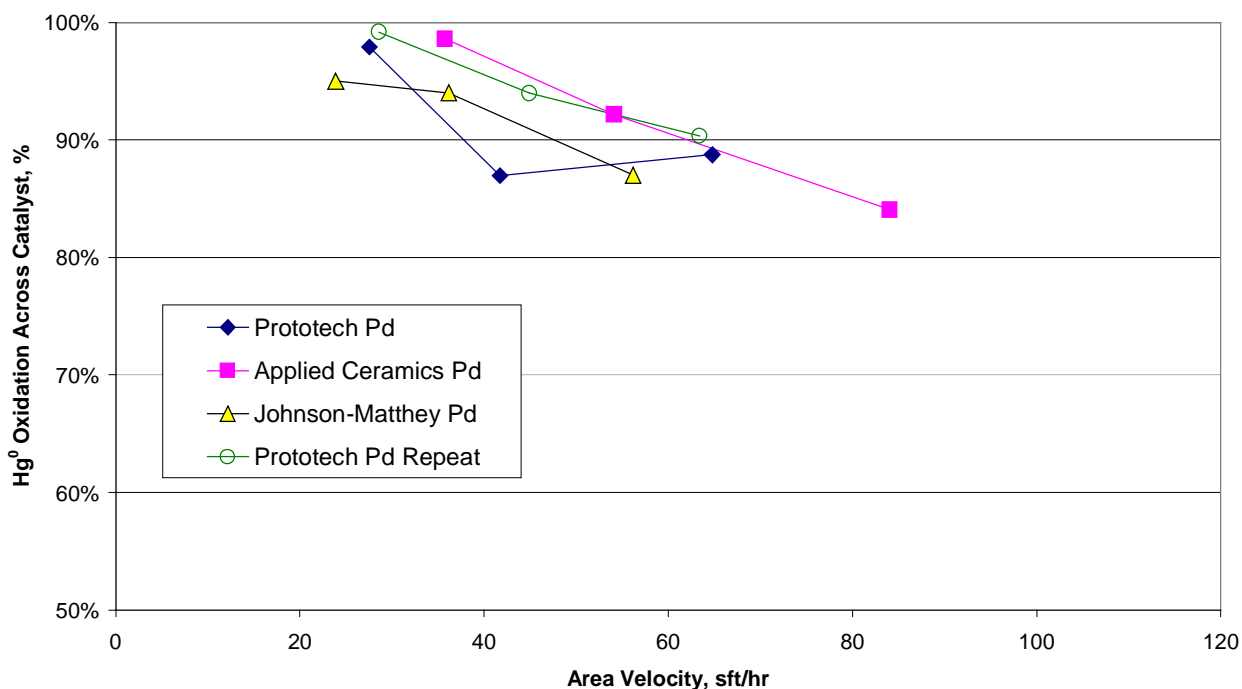


Figure 1. Catalyst Hg⁰ Oxidation Activity Results from the Current Quarter at Simulated Monticello Plant Gas Conditions

Figure 2 shows the data from the MHI catalyst repeat tests conducted during the quarter, with the previous MHI and Argillon SCR catalyst data added to the plot. In the original MHI data, the oxidation value for the MHI catalyst at the lowest area velocity value appeared to be erroneous, for the same reason as described above for the middle data point for the Prototech Pd #1. The oxidation percentage at the lowest area velocity value should be higher, rather than lower than the value at the middle area velocity value. However, in the repeat test, the expected trend was seen, with activity decreasing as area velocity increased. The differences in performance between

the Argillon and MHI catalysts are relatively minor, particularly at the lower area velocity values.

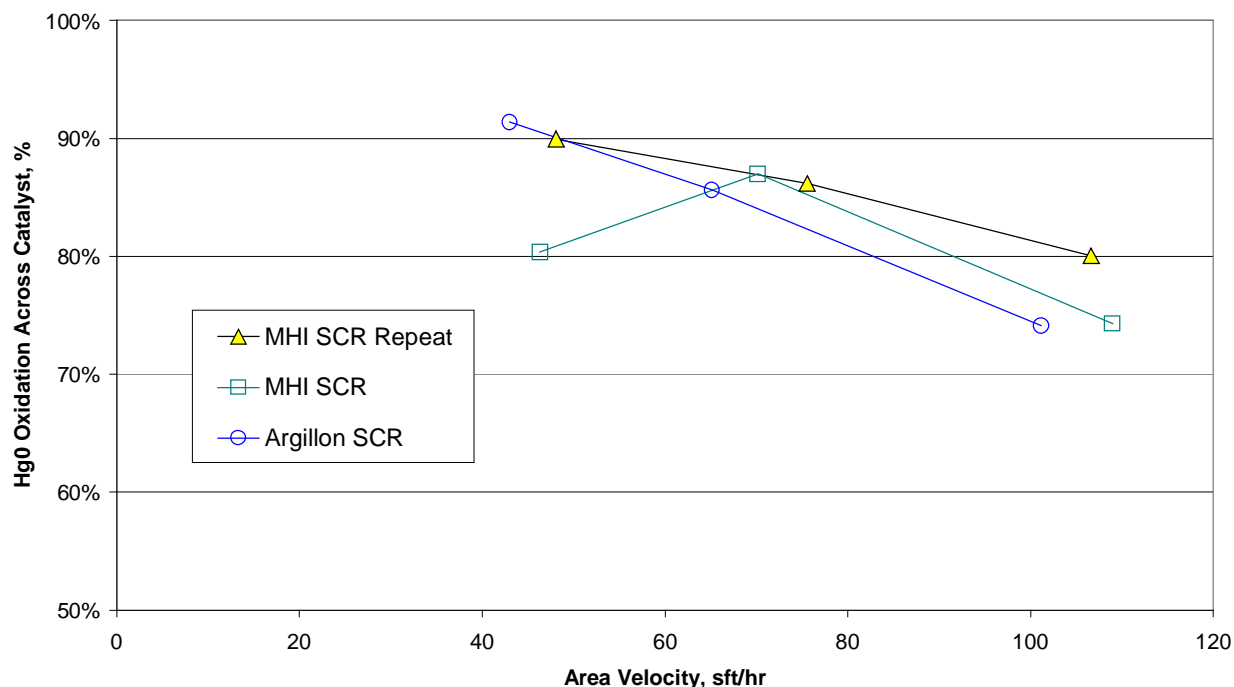


Figure 2. Catalyst Hg⁰ Oxidation Activity from the Previous Quarter at Simulated Monticello Plant Gas Conditions

Based on these results, it appears that Pd #1 catalysts from any of the three possible suppliers will perform similarly, as should SCR catalyst from either of the two suppliers considered. It would be difficult to clearly distinguish between the potential suppliers of these catalyst types based on the data available, so these decisions may be based on other factors such as promised catalyst delivery date, catalyst cost, and/or catalyst vendor cost sharing.

Pilot Wet FGD Tests at CCS

The completed pilot wet FGD skid was shipped from the fabricator in Austin, Texas to CCS on July 2, and the skid was installed and started up at CCS the following week. The wet FGD system is sized to treat all of the flue gas exiting a single catalyst compartment. The design basis and a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system were included in a previous technical progress report for this project.⁶

Over the following two weeks, the pilot wet FGD system was operated for a series of day shift tests (about 10-12 hours each) downstream of each catalyst compartment, with separate tests being conducted with magnesium-enhanced lime (Mg-lime) and limestone reagents. Mg-lime tests were conducted using the CCS full-scale FGD reagent, while the limestone tests were

conducted using dry-ground limestone (90% minus 325 mesh) that was slurried in plant water in the pilot FGD reagent storage tank. Mg-lime tests were conducted in a natural sulfite oxidation mode, while the limestone reagent tests were conducted in a forced oxidation mode, with FGD liquor sulfite concentrations being controlled below 1 mmol/l (80 mg/l). The FGD reaction tank was not drained between tests. Instead, each test was begun with the FGD slurry remaining from the previous test in the reaction tank. It was felt that this would be better than starting each day with fresh slurry, as the previous days' slurries should have been near steady state with respect to concentrations of chlorides, mercury, and other dissolved species. It was felt that most other potentially important parameters (e.g., pH, sulfite concentration) would reach steady state values soon after startup each day depending on the reagent makeup and pilot unit control parameters.

Wet FGD tests were conducted downstream of the two more active catalysts at CCS, the palladium-based (Pd #1) and carbon-based (C #6) catalysts. Because the fly-ash-based catalyst (SBA #5) appeared to be plugged with fly ash buildup and had little mercury oxidation activity, that catalyst was removed, leaving one empty chamber in the pilot unit. This empty chamber provided the opportunity to conduct baseline (no catalyst) tests with both the Mg-lime and limestone reagent chemistries.

FGD outlet mercury concentration and speciation data were measured by SCEM. A single SCEM was used to measure the normal catalyst inlet and catalyst outlet (FGD inlet) locations, and the new FGD outlet location for both total and elemental mercury concentrations. This proved to be a shortcoming in the test design, for two reasons. One is that it proved to be difficult to collect all six data sets in a contemporaneous manner. As an example, many hours typically elapsed between when the catalyst inlet total mercury concentrations were measured (normally the first parameter measured) and when the FGD outlet elemental mercury concentrations were measured (normally the last). Changes in flue gas mercury concentrations over that period could have impacted measured FGD performance.

The second reason this proved to be a shortcoming is that a temporary mercury sampling set up was used at the FGD outlet to connect that location to the normal catalyst pilot sampling system. This temporary system proved to be problematic, such that a number of the test results for mercury capture across the wet FGD are suspect. For several days, scrubber outlet data are questionable or not available because of poor recovery of mercury in QC spikes from the scrubber outlet location. In addition, episodes of gold column contamination in the mercury SCEM invalidated some mercury data.

Because of these issues in measuring FGD outlet mercury concentrations, and because of schedule and budget constraints, high quality data are not available for mercury removal across the pilot FGD system for all of the desired conditions. Table 2 summarizes the reportable results from this effort. For the first five rows of data, the wet FGD outlet data are believed to be biased low due to mercury losses in the temporary sample delivery system from the FGD outlet to the permanent sample delivery system from the oxidation catalyst pilot unit. Evidence of this bias was seen in poor recovery of mercury spikes made into the sample gas immediately upstream of the sample conditioning impingers at the wet FGD outlet location. Evidence of the low bias is also seen in the elemental mercury concentration data from the FGD outlet. For these five tests, apparent elemental mercury removal across the wet FGD system ranged from 36% to 80%,

Table 3. Summary of Gas Phase Mercury Data from Wet FGD Tests

Catalyst Type	FGD Reagent	Date	Catalyst Inlet Hg, mg/Nm ³ *			Inlet Total Hg Oxidation, %	Catalyst Outlet Hg, mg/Nm ³			Outlet Total Hg Oxidation, %	Hg ⁰ Oxidation Across Catalyst, %	Scrubber Outlet Hg, mg/Nm ³			Hg Removal Across FGD, %		
			Total	Hg ⁰	Hg ⁺²		Total	Hg ⁰	Hg ⁺²			Total	Hg ⁰	Hg ⁺²	Total	Hg ⁰	Hg ⁺²
Baseline (no catalyst)	Mg-lime	7/11/2004	-	-	-	-	16.5	9.95	6.53	40%	-	6.40**	6.39	0.01	61%	36%	100%
Baseline	Mg-lime	7/12/2004	-	-	-	-	14.5***	8.55	5.95	41%	-	4.30	4.04	0.26	70%	53%	96%
Baseline	Mg-lime	7/13/2004	-	-	-	-	14.4	8.48	5.93	41%	-	2.05	1.69	0.35	86%	80%	94%
Carbon #6	Mg-lime	7/14/2004	13.0	6.75	6.29	52%	12.8	4.46	8.33	65%	34%	1.13	0.99	0.14	91%	78%	98%
Carbon #6	Limestone	7/17/2004	18.3	10.4	7.93	57%	17.4	3.64	13.7	79%	65%	2.07	1.79	0.28	88%	51%	98%
Pd #1	Limestone	7/19/2004	18.0	11.9	6.05	66%	17.4	2.71	14.7	84%	77%	3.73	3.76	-0.03	79%	-39%	100%
Pd #1	Mg-lime	7/20/2004	16.9	10.5	6.46	62%	15.9	2.57	13.3	84%	75%	4.98	4.56	0.42	69%	-77%	97%
Carbon #6	Mg-lime	7/21/2004	19.5	10.9	8.55	56%	18.7	3.65	15.1	81%	67%	4.25	4.01	0.24	77%	-10%	98%

*Note: 1.0 µg/Nm³ = 0.66 lb Hg/10¹² Btu heat input

**Values shaded in gray are believed to be biased low due to mercury losses in the sample delivery system for the SCEM

***Estimated value

whereas no removal would be expected. Thus, the low bias was most likely of a similar order of magnitude.

For the final three rows of data, the temporary sample delivery system was upgraded with a new, higher wattage heat traced sample line, after which the spike recoveries improved to acceptable levels (typically $\pm 10\%$ of 100% recovery). For all three of these tests, the average elemental mercury removal was negative, indicating some mercury re-emissions.

The objective of the wet FGD pilot tests was to determine if the catalytically oxidized mercury could be removed at high efficiency. Mercury removal could be limited by two potential effects. One potential limitation is that a form of oxidized mercury could be produced by the catalyst that is less water-soluble than mercuric chloride, but is still removed by the KCl impinger in the Hg SCCEM train. Thus, such an alternate form would still be measured as being oxidized. A less soluble form of mercury may not be scrubbed at high efficiency in a wet FGD system. In such a case, the FGD outlet flue gas would contain significant concentrations of oxidized mercury as well as elemental mercury.

All eight data sets in Table 2 show that this is not the case. Little oxidized mercury was found in the FGD outlet flue gas from any of the tests, and observed oxidized mercury percentages were all well above 90%. Even for the five tests where the outlet mercury concentrations were biased low, because the oxidized mercury fraction is measured by the difference of the total and elemental mercury concentrations, and both should see the same low bias, it is clear that there was very little oxidized mercury in the outlet gas.

Another limitation on mercury removal by the wet FGD system would be re-emissions, where a portion of the oxidized mercury scrubbed undergoes reduction reactions in the FGD liquor, forming insoluble elemental mercury that is released into the scrubber outlet gas. Because of the low bias in the FGD outlet gas measurements, it is not possible to quantify re-emission across the FGD for the first five tests. Re-emissions are quantified as an increase in elemental mercury concentration measured across the FGD absorber, and for these tests the elemental mercury concentrations decrease due to the apparent low bias caused by the sample delivery system.

The remaining three test results, with good mercury recoveries, show evidence of re-emissions, with the FGD outlet flue gas containing 0.4 to 2.0 $\mu\text{g}/\text{Nm}^3$ higher elemental mercury concentrations than the inlet. Mercury re-emissions are believed to occur by reactions of absorbed oxidized mercury with sulfite ion in the FGD liquor, and re-emissions have been measured to frequently occur across Mg-lime FGD systems because they operate at elevated liquor sulfite concentrations. It is surprising that re-emissions were measured for the limestone condition on July 19. However, it should be noted that an hour elapsed between when the FGD outlet and catalyst outlet elemental mercury concentrations were measured. The observed re-emissions could in part be due to temporal variations in total and elemental mercury concentrations produced from the boiler.

Also, subsequent wet FGD tests being conducted as this report is being prepared have led to an observation that carryover of FGD liquor and/or solids, such as during upper mist eliminator washes, can lead to high biases in measured FGD outlet mercury concentrations. It is possible

that, after the sample delivery system mercury losses were corrected, the FGD outlet total and elemental mercury concentration data could have been biased high by scrubber carryover.

The results of this testing did not provide as much information as was hoped about the ability to scrub catalytically oxidized mercury from flue gas in a conventional wet FGD system. It is quite apparent that there is not a problem with forming oxidized mercury species that are not scrubbed at high efficiency; all of the FGD outlet mercury data show very little oxidized mercury in the FGD outlet flue gas. However, the results are not conclusive about mercury re-emissions when scrubbing the catalytically oxidized mercury. Mercury re-emissions could not be quantified for the first five test results presented. While re-emissions were indicated for the latter three test results, there are potentially confounding effects that may have overstated these re-emissions.

During the tests, FGD slurry samples were collected, preserved, and analyzed off site for routine FGD species concentrations. These results are summarized in Table 4.

Table 4. Analyses of FGD Samples from Pilot Wet FGD Tests at CCS

Test Description	Baseline Mg-Lime	Mg-Lime Carbon #6	Mg-Lime Carbon #6	Limestone Forced Ox. Carbon #6	Baseline Limestone Forced Ox.	Limestone Forced Ox. Pd #1	Mg-Lime Pd #1	Mg-Lime Carbon #6
Date	7/13/04	7/14/04	7/14/04	7/17/04	7/18/04	7/19/04	7/20/04	7/21/04
Time	17:00	16:30	19:30	15:15	17:30	18:30	17:45	15:45
pH	6.6	6.6	6.43	na*	5.96	5.81	6.49	6.56
Temperature, °C	55.1	56.1	55	na	55.1	55.2	na	na
Wt% Solids	10.8	9.9	10.2	12.1	12.5	12.9	15.0	15.9
Slurry Liquor Data:								
Ca ⁺⁺ , mg/L	512	500	496	516	512	497	518	511
Mg ⁺⁺ , mg/L	2,994	3,045	3,358	3,635	3,479	3,432	3,261	3,391
Cl ⁻ , mg/L	1,095	986	1,166	1,138	1,156	1,207	1,160	1,144
CO ₃ ⁼ , mg/L	185	187	191	51.6	64.8	97.8	176	179
SO ₃ ⁼ , mg/L	500	467	587	2.7	<0.9	2.4	727	643
SO ₄ ⁼ , mg/L	16,301	16,349	18,030	18,991	19,058	19,423	17,781	17,108
Slurry Solids Data:								
Ca, mg/g	258	264	267	221	230	219	222	229
Mg, mg/g	1.2	1.9	1.0	0.7	1.0	0.7	1.0	0.7
SO ₃ , mg/g	378	369	364	12.0	11.0	10.5	28.2	50.2
SO ₄ , mg/g	631	640	645	530	528	532	535	540
CO ₃ , mg/g	8.3	7.5	8.0	7.5	9.0	6.2	6.6	6.0
Inerts, wt%	0.33	0.08	0.12	0.73	0.82	0.85	0.85	0.56

*na – value not available

The results in Table 4 are as expected: the weight percent solids levels in the FGD recirculating slurry were typically in the target range of 10 to 15 wt%, and chlorides were about 1000 to 1200 mg/l (approximately equal to ppm) in the liquor. The Mg-lime tests showed sulfite concentrations in the liquor in the range of 500 to 700 ppm, while the limestone forced oxidation

tests showed low sulfite concentrations of 2.7 mg/l or less. The solids analyses showed that the Mg-lime tests produced a mixture of sulfite and sulfate solids, while the limestone forced oxidation tests produced gypsum with a purity of about 95% (dry basis).

The FGD liquor and solids samples are also being analyzed for mercury content. These results, when available, will be used to construct an approximate mercury balance around the wet FGD pilot. It is hoped that the mercury balance results will provide a better indication of overall mercury capture by the wet FGD system. The FGD liquor and solids mercury concentration data and the mercury balance results should be available for presentation in the next quarterly technical progress report for this project.

CONCLUSION

Based on the laboratory catalyst screening tests results to date, it appears that the four catalysts to be tested at Monticello should include the Prototech gold, Carbon #6, Pd #1 from one of three potential suppliers, and one of two candidate SCR catalysts. It would be difficult to clearly distinguish between the three Pd #1 suppliers and the two SCR catalysts based on the laboratory catalyst activity data available, so this decision was based on other factors, such as catalyst delivery schedule and net cost to the project. Correspondingly, it was decided to test Pd #1 catalyst from Johnson Matthey and SCR catalyst from MHI for the upcoming Monticello mercury oxidation catalyst pilot tests.

The pilot wet FGD tests conducted at CCS represented the first use of this pilot wet FGD system to measure mercury control performance downstream of the oxidation catalysts. In spite of mercury concentration measurement difficulties encountered, it was obvious in all of the test results that oxidized mercury formed across the catalysts can be absorbed by a wet FGD system at high efficiency, in either Mg-lime or limestone forced oxidation configurations. Overall mercury capture percentages of 70 to 80% were measured in these tests. FGD outlet oxidized mercury concentrations representing 6% or less of the inlet oxidized mercury.

The results of these tests were less decisive in quantifying another potential mechanism for limiting the capture of catalytically oxidized mercury in wet FGD systems: mercury re-emissions. The apparent re-emissions levels were biased low in the first five of eight test results presented, by the temporary sample delivery system used by the mercury SCEM for the wet FGD outlet location. Results for the other three tests may have been biased high by potential carry over of FGD liquor and/or solids into the sample delivery system.

Lessons were learned from the pilot wet FGD tests at CCS that can be used to improve data quality in the future. The primary lesson learned is that it would be best to use two mercury SCEMs to quantify catalyst and FGD performance, with one SCEM dedicated to the FGD outlet location. This would minimize sample line length requirements, reducing tendencies for mercury losses in the sample delivery system, and would allow simultaneous measurements of catalyst outlet/FGD inlet and FGD outlet flue gas mercury concentrations.

REFERENCES

1. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, October 1, 2002 – December 31, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. January 2003.
2. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, July 1, 2002 – September 30, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. October 2002.
3. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, March 1, 2002 – June 30, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. July 2002.
4. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, January 1, 2002 – March 31, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. April 2002.
5. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems, Final Report, Phase II*, U.S. Department of Energy Cooperative Agreement Number DE-AC22-95PC95260, URS Corporation, Austin, Texas 78729. June 2001.
6. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, January 1, 2004 – March 31, 2004. Cooperative Agreement No. DE-FC26-04NT41992, URS Corporation, Austin, Texas 78729. April 2004.